	Type	Hits	Search Text	DBs
19	BRS	79	(piezoelectric or electrostrictive or magnetostrictive or electromechanical) not (((piezoelectric or magnetostritive or electromechanical) same biaxial) or ((piezoelectric or magnetostritive or electromechanical) same biaxial) or ((piezoelectric or magnetostritive or electromechanical) same biaxially) or ((piezoelectric or magnetostritive or electromechanical) same biaxially) or ((piezoelectric or magnetostritive or electromechanical) and biaxial$2 not (((piezoelectric or magnetostritive or electromechanical) same biaxial) or ((piezoelectric or magnetostritive or electromechanical) same biaxial) or ((piezoelectric or magnetostritive or electromechanical) same biaxially) or ((piezoelectric or magnetostritive or electromechanical) same biaxially))) or	USPAT; US-PGPUB; EPO; JPO; DERWENT; IBM_TDB
20	BRS	141	oxide adj1 film same piezoelectric	USPAT
21	BRS	69	oxide adj1 layer same piezoelectric not zinc adj1 oxide	US-PGPUB; EPO; JPO; DERWENT; IBM_TDB

	Time Stamp	Comments	Error Definition	Errors
19	2002/05/24 10:20			0
20	2002/06/10 16:03			0
21	2002/06/11 08:22			0

	Type	L #	Hits	Search Text	DBs	Time Stamp	Comments
1	BRS	L33	179	oxide adj1 film same piezoelectric not zinc adj1 oxide not oxide adj1 layer	US-PGPUB; EPO; JPO; DERWENT; IBM_TDB	2002/06/11 08:56	
2	BRS	L34	69	oxide adj1 film same piezoelectric not zinc adj1 oxide not oxide adj1 layer	USPAT	2002/06/11 09:05	
3	BRS	L35	21	oxide adj1 (film or layer) same piezoelectric not zinc adj1 oxide	USOCR	2002/06/11 09:06	

Nov. 1, 1949 H. R. MOULTON 2,486,968

MEANS AND METHOD OF ALTERING THE FREQUENCY
OF PIEZOELECTRIC CRYSTALS
Filed Nov. 22, 1943

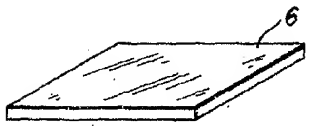

Fig. 1

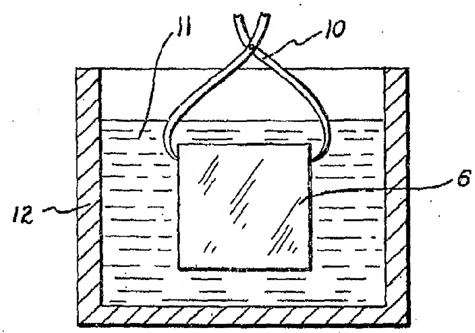

Fig. 2

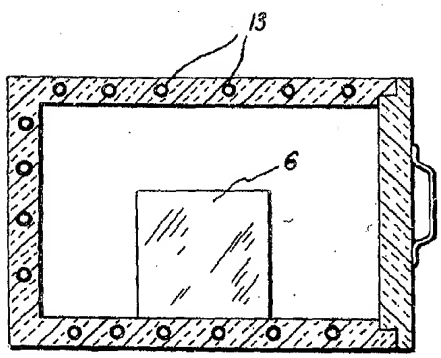

Fig. 3

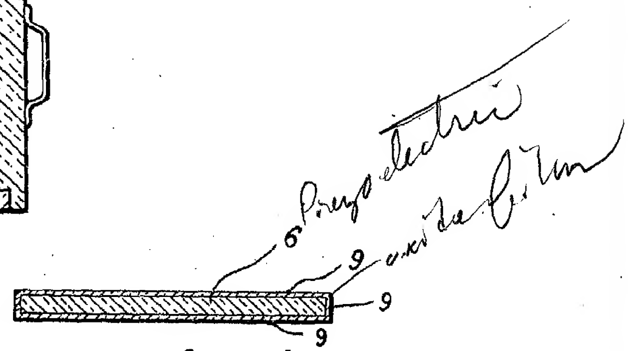

Fig. 4

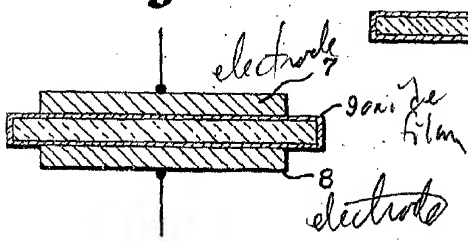

Fig. 5

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MEANS AND METHOD OF ALTERING THE FREQUENCY OF PIEZOELECTRIC CRYSTALS

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Application November 22, 1943, Serial No. 511,228

22 Claims. (Cl. 171—327)

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This invention relates to piezoelectric crystals and has particular reference to the provision of novel means and method of controlling the frequencies of said crystals.

One of the principal objects of the invention is to provide novel means and method of piezoelectric crystal fabrication whereby the resultant frequencies of the crystals may be more easily and more accurately controlled.

Another object is to provide novel means and method of altering the frequencies of the crystals whose inherent physical dimensions are such as to have higher frequencies than desired whereby the said frequencies may be lowered a controlled amount.

Another object is to provide novel means and method of reclaiming crystals whose frequencies through manufacturing errors have been raised above the desired value.

Another object is to provide novel means and method of altering the frequencies and oscillations of the crystal with substantially no change in the inherent stability of said crystals.

Another object is to provide novel means and method of lowering the frequencies of crystals with substantially no alteration of the physical inherent dimensions or shapes of the fabricated crystals.

Another object is to provide novel and simplified means and method of more positively controlling the frequencies of oscillations of the crystals thereby greatly facilitating and providing ease of fabrication.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawings and it will be apparent that many changes in the details of construction and arrangement of parts and in the steps of the processes may be made without departing from the invention as expressed in the accompanying claims. I, therefore, do not wish to be limited to the exact details of construction, arrangement of parts and steps of the method shown and described as the preferred forms only have been given by way of illustration.

Referring to the drawings:

Fig. 1 is a perspective view of one form of piezoelectric crystal oscillator to which the invention is to be applied;

Fig. 2 is a schematic view illustrating one step of the method embodying the invention;

Fig. 3 is a view generally similar to Fig. 2 of a further step of the method;

Fig. 4 is a sectional view of the crystal having

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the coating embodying the invention applied thereto; and

Fig. 5 is a diagrammatical view of the crystal and mounting therefor.

It is well known that in order to obtain a piezoelectric crystal which has a given frequency of oscillation that the physical dimensions of the crystal must be very carefully controlled during the fabrication thereof. Such physical dimensions constitute the over all size and thickness of the crystal with the said thickness being very carefully controlled dimensionally throughout the area of the crystal. It is also well known that in order to obtain higher frequencies of oscillation the crystals must be reduced in thickness. It is quite apparent that great care must be exercised in obtaining the desired uniformity of thickness in order to obtain the desired frequencies of oscillation on large scale production. This has introduced considerable difficulty as a very slight reduction of the thickness beyond that required for a particular frequency of oscillation will increase said frequency and thereby render the crystal impractical for use for that particular frequency. This difficulty becomes more pronounced in the case of high frequency crystals such as are used in short wave and ultra short wave equipment and therefore introduce much more difficulty in producing such crystals than in the case of low frequency crystals. Even with crystals having medium frequencies of oscillation great care must be taken not to grind too thin.

One of the prime objects, therefore, of the present invention is to overcome the above difficulty by providing novel means and methods of changing or altering the frequency of a crystal from that of the inherent frequency of the immediate crystal body in a simple and efficient manner whereby a more positive and flexible control of the frequency may be obtained.

Referring more particularly to the drawings wherein like characters of reference designate like parts of the several views, a piezoelectric crystal 6 such as shown is first formed to the approximate size and thickness required with the said oscillations of said crystal being slightly higher than the immediate required frequency of oscillation. The crystal 6 is formed in the usual manner by known prior art methods and is intended to be used between suitable electrodes 7 and 8 as shown diagrammatically in Fig. 5. The crystal 6, in order to obtain exactness in the frequency of oscillation, is then coated throughout all of its outer surfaces or throughout one or

more of said surfaces to provide a thin film or coating 9 of material thereon which will lower the frequency of oscillation of said crystal. The amount of lowering of the frequency of oscillation depends upon the thickness of coating 9 or the number of coatings applied thereto and the material of the coating.

The coating may be applied as shown diagrammatically in Fig. 2 by grasping the crystal 6 in a suitable holder 10 and dipping said crystal into the coating solution 11 in a suitable container 12.

It is to be understood that the said coating may be applied to the crystal by spinning, brushing, spraying or any other suitable method by which a substantially uniform coating may be applied.

If it is desired to apply the coating to one of the surfaces of the crystal the other surfaces may be supplied with a soluble or removable coating which is not attacked by the coating solution 11.

The crystal 6 after having the proper thickness of coating 9 applied thereto is preferably heated to set the coating. This may be accomplished by placing the coated crystal 6 within a suitable heat chamber such as shown diagrammatically in Fig. 3. In this particular instance the chamber is provided with a plurality of electrical heating units 13 by which the desired amount of heat may be generated internally of the chamber. It is to be understood that other methods of heat may be used.

The solution 11 may be conveniently produced by mixing 45 parts by volume of ethyl alcohol, 45 parts by volume of ethyl acetate, 5 parts per volume of tetra-ethyl-ortho-silicate and after thorough stirring 5 parts of concentrated hydrochloric acid in aqueous solution. While hydrochloric acid is mentioned other volatile inorganic acids may be used such as hydrobromic acid, or organic acids, such as formic acid, chloracetic acid, etc. may be used. Other solvents such as butyl alcohol, iso-propyl alcohol, monoethyl-ester-of-monoethylene-glycol and similar water miscible solvents may be used in preparation of different solvents. While the above proportions are shown by way of example to be a good workable solution, it is to be understood that the relative proportion of the various ingredients, whatever solvents be used, may be varied. For example, a solution consisting of 85 parts of ethyl alcohol, 5 parts hydrochloric acid and 10 parts of tetraethyl-ortho-silicate may be used whereby a thicker coating is obtained. If a thinner coating is desired the content of the most active ingredient, namely, tetra-ethyl-ortho-silicate may be reduced. To facilitate application other solvents as described above may be used and in such cases the content of tetra-ethyl-ortho-silicate would be modified in order to provide a coating of the desired thickness.

A similar coating of a titanium compound may be produced by applying in a similar manner a coating forming solution made by the addition of titanium tetra-chloride to ethyl alcohol. Other alcohols may be used in place of the ethyl alcohol. Other alcohols may be used and other solvents mixed therewith, before, during or after the addition of titanium tetra-chloride.

The lower order alcohols, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, secondary butyl alcohol, the water miscible Cellosolves and their derivatives, water, 1-4-dioxane, or in general water miscible organic solvents may be used, the proportion being dependent upon the conditions of application. An example of a solution which has been found to produce good results is made by adding slowly with stirring 5 grams of titanium tetrachloride to 100 grams of ethyl alcohol. The addition must be made slowly because the reaction is rather violent. A pale yellow liquid results which when applied in a thin layer and dried deposits a thin, coherent, hard, durable and rigid layer consisting substantially of titanium oxide which like the silicon containing layer above described lowers the frequency of the piezoelectric crystal to which it has been applied, the extent of lowering depending upon the thickness of the coating and the number of coatings applied.

Other suitable decomposable compounds of titanium such as titanium tetra-bromide may be used with substantially the same solvents as used in Tables III and IV and in substantially the same proportions. Composite solutions containing both tetra-ethyl-ortho-silicate and titanium tetra-chloride may be used, whereby a layer or coating containing intermingled silicon dioxide and titanium dioxide in any desired proportions may be produced.

Table I

	Parts by weight
Ethyl alcohol	0–90
Ethyl acetate	0–50
Tetra-ethyl-ortho-silicate	0.1–10
Hydrochloric acid	0.1–10
Butyl alcohol	0–90
Monoethyl ether of mono-ethylene glycol	0–90

Table II

	Parts by weight
Volatile water miscible organic vehicle	Up to 99.8
Tetra-ethyl-ortho-silicate	0.1 to 10
Acid	0.1 to 10

Table III

	Parts by weight
Ethyl alcohol	0 to 99.9
Titanium tetra-chloride	0.1 to 20
Methyl alcohol	0 to 99.9
Butyl alcohol	0 to 20
Monoethyl ether of monoethylene glycol	0 to 20

Table IV

	Parts by weight
Ethyl alcohol	0 to 99.8
Titanium tetra-chloride	0.1 to 10
Volatile, water miscible organic vehicle	0 to 90
Tetra-ethyl-ortho-silicate	0.1 to 10
Acid	0 to 10

Table I shows proportions of various ingredients which have given useful results by the deposition of a silicon dioxide layer.

Table II shows, more generally, the proportions of volatile, water miscible organic vehicle, tetra-ethyl-ortho-silicate, and acid which have been found useful in producing solution-deposited silicon dioxide layers.

Table III shows the proportions of various ingredients which have given useful results by the solution deposition of a titanium dioxide layer.

Table IV shows the proportions of various ingredients which have been found useful in solution depositing layers containing both silicon dioxide and titanium dioxide.

It is to be understood that the invention herein disclosed is particularly adaptable to reclaiming crystals which have been erroneously reduced

to a smaller dimension than desired for obtaining a particular frequency of oscillation, but if it is desired to obviate the extreme accuracy of fabrication in forming such piezoelectric crystals the said crystals may be reduced slightly beyond the dimension required and may thereafter be made to oscillate at the required crystal frequency by the coating treatment above described.

The above provides a simple and efficient and extremely accurate method of obtaining the required frequency of oscillation.

Crystals coated in the above manner are permanently resistant to weathering and mechanically stable.

The piezoelectric crystals referred to herein may be any of the commonly known type such as quartz, tourmaline, etc.

From the foregoing description it will be seen that simple, economical and efficient means have been used to accomplish all of the objects and advantages of the invention.

Having described my invention, I claim:

1. A piezoelectric crystal having upon a surface thereof a thin adherent layer of silicon dioxide of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

2. A piezoelectric crystal having upon a surface thereof a solution deposited thin adherent layer consisting substantially of silicon dioxide of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

3. A piezoelectric crystal having upon a surface thereof a thin adherent film or layer of silicon compound of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

4. A piezoelectric crystal having upon a surface thereof a solution deposited thin adherent layer of silicon compound of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

5. A piezoelectric crystal having upon a surface thereof a thin adherent layer of titanium dioxide of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

6. A piezoelectric crystal having upon a surface hereof a solution deposited thin adherent layer of titanium compound of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

7. A piezoelectric crystal having upon a surface thereof a thin adherent layer of titanium dioxide and silicon dioxide of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

8. A piezoelectric crystal having upon a surface thereof a solution deposited thin adherent layer containing titanium dioxide and silicon dioxide of a controlled thickness, said thickness being proportionate to the frequency of oscillation of the crystal desired.

9. A piezoelectric crystal having upon a surface thereof a thin adherent layer resulting from the coating of said surface with a solution containing:

	Parts by weight
Ethyl alcohol	0–90
Ethyl acetate	0–50
Tetra-ethyl-ortho-silicate	0.1–10
Hydrochloric acid	0.1–10
Butyl alcohol	0–90
Monoethyl ether of monoethylene glycol	0–90

and with said layer being of a controlled thickness proportionate to the desired frequency of oscillation of the crystal.

10. A piezoelectric crystal having upon a surface thereof a thin adherent layer resulting from the coating of said surface with a solution containing:

	Parts by weight
Volatile water miscible organic vehicle	Up to 99.8
Tetra-ethyl-ortho-silicate	0.1 to 10
Acid	0.1 to 10

and with said layer being of a controlled thickness proportionate to the desired frequency of oscillation of the crystal.

11. A piezoelectric crystal having upon a surface thereof a thin adherent layer resulting from the coating of said surface with a solution containing:

	Parts by weight
Ethyl alcohol	0 to 99.9
Titanium tetra-chloride	0.1 to 20
Methyl alcohol	0 to 99.9
Butyl alcohol	0 to 20
Monoethyl ether of monoethylene glycol	0 to 20

and with said layer being of a controlled thickness proportionate to the desired frequency of oscillation of the crystal.

12. A piezoelectric crystal having upon a surface thereof a thin adherent layer resulting from the coating of said surface with a solution containing:

Ethyl alcohol	0 to 99.8
Titanium tetra-chloride	0.1 to 10
Volatile, water miscible organic vehicle	0 to 90
Tetra-ethyl-ortho-silicate	0.1 to 10
Acid	0 to 10

and with said layer being of a controlled thickness proportionate to the desired frequency of oscillation of the crystal.

13. The method of modifying the natural frequency of oscillation of a piezoelectric crystal comprising depositing a coating from a solution containing:

	Parts by weight
Ethyl alcohol	0–90
Ethyl acetate	0–50
Tetra-ethyl-ortho-silicate	0.1–10
Hydrochloric acid	0.1–10
Butyl alcohol	0–90
Monoethyl ether of mono-ethylene glycol	0–90

controlling the thickness of the coating in proportion to the desired frequency of oscillation of the crystal, and thereafter heating said coated article to set the coating.

14. The method of modifying the natural frequency of oscillation of a piezoelectric crystal comprising depositing a coating from a solution containing:

	Parts by weight
Volatile water miscible organic vehicle	Up to 99.8
Tetra-ethyl-ortho-silicate	0.1 to 10
Acid	0.1 to 10

controlling the thickness of the coating in proportion to the desired frequency of oscillation of the crystal, and thereafter heating said coated article to set the coating.

15. The method of modifying the natural frequency of oscillation of a piezoelectric crystal

comprising depositing a coating from a solution containing:

	Parts by weight
Ethyl alcohol	0 to 99.9
Titanium tetra-chloride	0.1 to 20
Methyl alcohol	0 to 99.9
Butyl alcohol	0 to 20
Monoethyl ether of monoethylene glycol	0 to 20

controlling the thickness of the coating in proportion to the desired frequency of oscillation of the crystal, and thereafter heating said coated article to set the coating.

16. The method of modifying the natural frequency of oscillation of a piezoelectric crystal comprising depositing a coating from a solution containing:

	Parts by weight
Ethyl alcohol	0 to 99.8
Titanium tetra-chloride	0.1 to 10
Volatile, water miscible organic vehicle	0 to 90
Tetra-ethyl-ortho-silicate	0.1 to 10
Acid	0 to 10

controlling the thickness of the coating in proportion to the desired frequency of oscillation of the crystal, and thereafter heating said coated article to set the coating.

17. The method of modifying the natural frequency of oscillation of a piezoelectric crystal comprising depositing a thin adherent coating of silicon dioxide and controlling the thickness of the coating in proportion to the frequency of oscillation desired.

18. A piezoelectric crystal having upon a surface thereof a thin adherent layer resulting from the coating of said surface with a solution containing a volatile, water miscible organic vehicle and a decomposable material selected from the group consisting of tetraethylorthosilicate, titanium tetrachloride, and mixtures thereof, the evaporation of the vehicle from the solution and the decomposition of the decomposable material, said layer being of a controlled thickness proportionate to the frequency of oscillation of the article desired.

19. A piezo-electric crystal comprising a substrate of piezo-electric material of a given frequency of oscillation greater than required for the resultant crystal, and a thin firmly-adherent layer on the surface of said substrate of a material which will reduce the frequency of oscillation of the substrate, said layer consisting substantially of a material selected from the group consisting of silicon compound, titanium compound and mixtures of silicon compound and titanium compound, the thickness of said layer being sufficient to reduce the frequency of oscillation of the substrate to the frequency desired for the resultant crystal.

20. A piezo-electric crystal comprising a substrate of piezo-electric material of a given frequency of oscillation greater than required for the resultant crystal, and a firmly adherent layer on the surface of said substrate of a material which will reduce the frequency of oscillation of the substrate, said layer consisting substantially

of a material selected from the group consisting of silicon dioxide, titanium dioxide and mixtures of silicon dioxide and titanium dioxide, the thickness of said layer being sufficient to reduce the frequency of oscillation of the substrate to the frequency desired for the resultant crystal.

21. The method of modifying the frequency of oscillation of a piezo-electric crystal comprising the steps of applying and forming on the surface of the piezo-electric crystal, said crystal having been initially cut to dimensions having a frequency of oscillation in excess of that desired for the final crystal, a liquid layer consisting of a water-miscible volatile organic solvent containing a controlled amount of a material that on decomposition will produce an oxide selected from the group consisting of silicon dioxide, titanium dioxide and mixtures of silicon and titanium dioxide, the amount of the decomposable material in said liquid layer being controlled according to the thickness of the oxide layer desired on evaporation of the solvent, and evaporating the solvent from said liquid layer so as to produce a dry layer of the oxide and with the thickness of said oxide layer being sufficient to reduce the frequency of oscillation of the crystal to the frequency desired for the coated crystal.

22. The method of modifying the frequency of oscillation of a piezo-electric crystal comprising the steps of applying to and forming on the surface of the piezo-electric crystal, said crystal having been initially cut to dimensions having a frequency of oscillation in excess of that desired for the final crystal, a liquid layer consisting of a water-miscible volatile organic solvent containing a controlled amount of decomposable material selected from the group consisting of tetraethylorthosilicate, titanium tetrachloride and mixtures thereof, the amount of the decomposable material in said liquid layer being controlled according to the thickness of the resultant layer desired on evaporation of the solvent, and evaporating the solvent from said liquid layer so as to produce a dry layer of the decomposition product of said decomposable material and with the thickness of said decomposition product being sufficient to reduce the frequency of oscillation of the crystal to the frequency desired for the coated crystal.

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